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**Author:** T. Toliński, A. Kowalczyk, M. Falkowski, K. Synoradzki, Grażyna  
Chełkowska, A. Hoser, S. Rols

**Citation style:** Toliński T., Kowalczyk A., Falkowski M., Synoradzki K.,  
Chełkowska Grażyna, Hoser A., Rols S. (2012). Electronic structure of CePtIn  
and LaPtIn compounds. "Acta Physica Polonica A" (Vol. 121, nr 5/6 (2012), s.  
1014-1018).



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# From Heavy Fermion and Spin-Glass Behavior to Magnetic Order in $\text{CeT}_4\text{M}$ Compounds

T. TOLIŃSKI<sup>a,\*</sup>, A. KOWALCZYK<sup>a</sup>, M. FALKOWSKI<sup>a</sup>, K. SYNORADZKI<sup>a</sup>, G. CHEŁKOWSKA<sup>b</sup>,  
A. HOSER<sup>c</sup> AND S. ROLS<sup>d</sup>

<sup>a</sup>Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

<sup>b</sup>Institute of Physics, Silesian University, Katowice, Uniwersytecka 4, 40-007 Katowice, Poland

<sup>c</sup>Helmholtz-Zentrum, Glienicker Straße 100, D-14109 Berlin, Germany

<sup>d</sup>Institut Laue Langevin, 6 rue Jules Horowitz, B.P. 156 F-38042, Grenoble Cedex 9, France

We report on the transitions between the ferromagnetic order, spin-glass behavior, heavy fermion and fluctuating valence state in a series of isostructural compounds  $\text{CeT}_4\text{M}$  ( $\text{T} = \text{Ni}, \text{Cu}$ ;  $\text{M} = \text{Al}, \text{Ga}, \text{Mn}$ ). The dilution of Ce or the T and M elements allowed us to follow the physical properties evolution employing the measurements of the heat capacity, dc magnetic susceptibility, frequency dependent ac magnetic susceptibility, magnetization relaxation, inelastic neutron scattering and also the X-ray photoemission spectroscopy. It is shown that the Mn rich compounds lean towards the spin glass behavior. For the compounds governed by the close to localization Ce 4*f* states the effect of the crystal electric field has been studied. It has been shown that the spin glass-like behavior can significantly influence the physics of the  $\text{CeT}_4\text{M}$  compounds.

PACS: 71.20.Lp, 71.27.+a, 75.30.Mb, 75.30.Cr, 75.50.Lk, 78.70.Nx

## 1. Introduction

Compounds containing the anomalous rare earths, e.g. Ce or Yb, can exhibit intriguing physical properties, which result mainly from the proximity of the *f* states to the Fermi level. This proximity implies an important role of the hybridization of the *f* electrons with the conduction electrons and the dynamical modification of the occupancy of the *f* states. Consequently, the Ce-based intermetallics can show unusual effects like: the effective mass enhancement (heavy fermions — HF), fluctuating valence (FV), impurity Kondo effect (IK), Kondo lattice (KL) formation, superconductivity with unconventional pairing mechanisms, ferromagnetism (FM), spin-glass (SG) behavior, quantum critical point (QCP) or the non-Fermi-liquid behavior (NFL) [1–10]. It is especially interesting and it is a challenge to observe a transformation between these various types of materials/effects. It requires to study the diluted systems, where one of the elements is gradually substituted by a different one. The resulting change of the internal (chemical) pressure can affect significantly the hybridization of the *f* states with the conduction electrons and the occupation of the *f* level. These parameters are usually studied within the Anderson model, which makes extensive use of the hopping term and the Coulomb repulsion [11].

The physical properties of the diluted Ce-based intermetallic compounds have been recently widely studied [12–15] and it has been shown that such gradual com-

position change does not have to lead to the continuous evolution of the properties between those characteristic of the border compounds but new effects can arise, e.g. by driving the system into the neighborhood of the quantum critical point [9, 10].

The interpretation of the experimental results is often ambiguous if the dilution initiates a change of the crystallographic structure. Our recent studies concern a group of compounds, which possess the same structure and space group and, moreover, the structure is stable when the alloying between the various starting compounds is carried out.

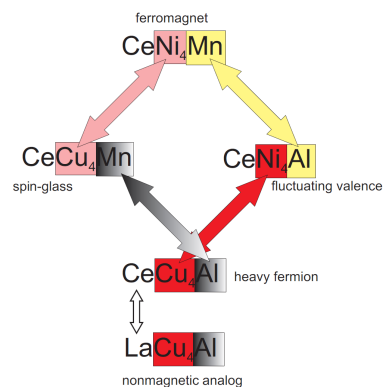


Fig. 1. Schematic representation of the compounds and the transitions studied.

A scheme presented in Fig. 1 illustrates the group of the studied materials and the arrows indicate the types of the studied transformations. By the dilution in  $\text{CeT}_4\text{M}$

\* corresponding author; e-mail: tomtol@ifmpan.poznan.pl

we understand here the graduate substitution of Ce, Ni, and Mn with La, Cu, and Al, respectively. This paper is divided into sections describing the most advanced of our studies of the various transitions depicted in Fig. 1. In a significant part a new or developed analysis of the results is presented.

## 2. Experimental details

The CeT<sub>4</sub>M compounds have been prepared by the induction melting of high purity elements in argon atmosphere. The crystal structure was controlled by the powder X-ray diffraction technique, using the Co  $K_\alpha$  radiation. For all the samples, the full-pattern Rietveld refinement corroborated the hexagonal CaCu<sub>5</sub>-type structure, space group  $P6/mmm$ .

Heat capacity measurements were carried out on the PPMS commercial device (Quantum Design) in the temperature range 1.9–300 K, by the relaxation method using the two- $\tau$  model. The magnetic and transport properties have been measured using the options of the PPMS device. In the case of the dc magnetic measurements the VSM option has been employed.

The inelastic neutron diffraction (INS) experiments were carried out on the IN4 time-of-flight instrument at the Institut Laue Langevin (ILL) in Grenoble using incident neutrons wavelength of 1.1 Å and 1.8 Å.

The X-ray photoemission spectra (XPS) were obtained using the Al  $K_\alpha$  source (1487.6 eV) with a Physical Electronics PHI 5700/660 Spectrometer, after breaking the sample directly in a vacuum.

## 3. The CeCu<sub>4</sub>Al–LaCu<sub>4</sub>Al transition

We start the discussion with the HF CeCu<sub>4</sub>Al compound and the gradual dilution of Ce with La. The properties of CeCu<sub>4</sub>Al are already well established. It is paramagnetic down to the lowest temperatures, it shows a large enhancement of the effective mass and the first excited energy level, resulting from the crystal electric field (CEF) splitting is about 60–90 K above the ground state [16–24]. In Fig. 2 the temperature dependence of the reciprocal magnetic susceptibility is presented for a few values of  $x$  in Ce<sub>1-x</sub>La<sub>x</sub>Cu<sub>4</sub>Al. The magnetic moments of the Ce ions are already well localized for  $x = 0$  and it is not expected that this will be significantly changed after the dilution with La. The main origin of the spread of the susceptibility curves (Fig. 2) is a change of the value of the temperature independent term  $\chi_0$ . This is well visible in the inset of Fig. 2, where the  $(\chi - \chi_0)^{-1}$  vs.  $T$  curves are plotted. All the curves nearly coincide in the entire temperature range studied. The remaining differences between the curves stem from the changes of the molecular field and CEF parameters. For increasing content of La one can expect a drop of the Ce–Ce interactions. This is really visible in the absolute values of the molecular field parameters, especially the parallel component (Table), which drops down to 6 mol/emu for

$x = 0.8$ . For lower  $x$  it is about 100 mol/emu with a spread of values, which may be due to the randomness of the Ce and La distribution on the 1a site (0, 0, 0). The calculations of the CEF contribution to the magnetic susceptibility have been carried out according to the Hamiltonian for the hexagonal point symmetry

$$H = B_2^0 O_2^0 + B_4^0 O_4^0, \quad (1)$$

where  $O_n^m$  and  $B_n^m$  are the Steven operators and CEF parameters, respectively. Based on the derived eigenenergies the calculation of the sum of the Curie and Van Vleck susceptibilities was carried out according to the equation

$$\chi^i = \frac{N(g_J\mu_B)^2}{Zk_B T} \left( \sum_{\substack{n,m \\ E_n=E_m}} |\langle n|J_i|m\rangle|^2 e^{-\frac{E_n}{k_B T}} + 2k_B T \sum_{\substack{n,m \\ E_n \neq E_m}} \frac{|\langle n|J_i|m\rangle|^2}{E_m - E_n} e^{-\frac{E_n}{k_B T}} \right), \quad (2)$$

where  $i$  is the  $x$ ,  $y$  and  $z$  component of the angular momentum,  $g_J$  is the Landé  $g$  factor,  $Z$  is the partition function,  $N$  is the Avogadro number and  $E_n$  are the energies of the wave functions above the ground state. For the polycrystalline samples the spatial averaging of the susceptibility components has to be carried out, i.e.  $\chi = n\chi_{\parallel} + (1 - n)\chi_{\perp}$ . The  $c$  axis states the quantization direction  $z$  and the  $\chi^i$  components perpendicular to the  $z$  direction are equal for the structure studied. In the presence of texture  $n$  can deviate from the ideal case of  $n = 1/3$ .

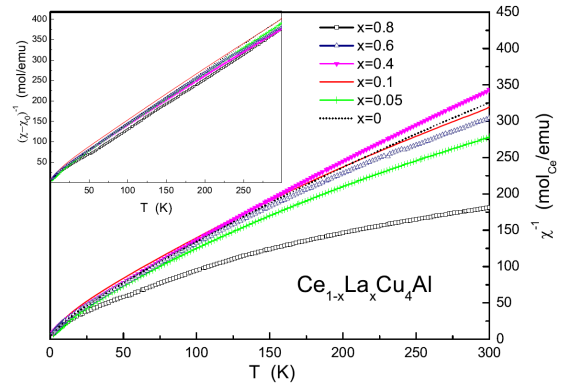


Fig. 2. Reciprocal magnetic susceptibility for Ce<sub>1-x</sub>La<sub>x</sub>Cu<sub>4</sub>Al. Inset:  $(\chi - \chi_0)^{-1}$  vs.  $T$ .

Figure 3 shows the example of the CEF analysis for several values of  $x$ . The values of the CEF parameters  $B_n^m$ , the molecular field parameters  $\lambda$  ( $\chi^{-1} = \chi_{\text{CEF}}^{-1} - \lambda$ ) and the temperature independent term  $\chi_0$  are listed in Table.

According to the Hamiltonian form the above parameters result in the pure  $\Gamma_7$ ,  $\Gamma_8$ , and  $\Gamma_9$  eigenstates, the first one ( $|\pm 1/2\rangle$ ) being the ground state. It stems from Table that the increase of the La content leads to the de-

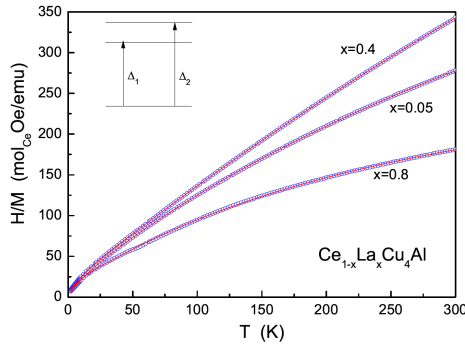


Fig. 3. Reciprocal magnetic susceptibility of  $\text{Ce}_{1-x}\text{La}_x\text{Cu}_4\text{Al}$  analyzed with the CEF model (Eq. (2)).

TABLE

Crystal electric field parameters for  $\text{Ce}_{1-x}\text{La}_x\text{Cu}_4\text{Al}$  obtained from the least squares fit with Eq. (2).

$x$	$\lambda_{\parallel}$ [mol/emu]	$\lambda_{\perp}$ [mol/emu]	$B_2^0$ [K]	$B_4^0$ [K]	$\chi_0 \times 10^{-4}$ [emu/mol]	$\Delta_1$ [K]	$\Delta_2$ [K]
0.0	-86	-2.56	3.01	-0.39	5.66	78	135
0.05	-77.8	-0.98	1.04	-0.30	10.8	37	96
0.1	-151	-5	4.12	-0.53	7.26	106	185
0.4	-75.3	-3.2	2.98	-0.36	3.99	75	126
0.6	-162	-3.7	4.31	-0.32	8.63	87	93
0.8	-5.8	-2.9	3.21	-0.22	28.8	71	87

crease of the interactions in the direction parallel to the  $c$  axis and enhancement of the temperature independent susceptibility. The first excited doublet, derived from the magnetic susceptibility analysis coincides with our previous observations of the CEF excitation (Fig. 4) in the inelastic neutron scattering for  $\text{CeCu}_4\text{Al}$  [21]. The shift of the spectrum for the non-magnetic analog  $\text{YCu}_4\text{Al}$  is due to the softening of the phonons energy due to the lower atomic mass of yttrium compared to cerium.

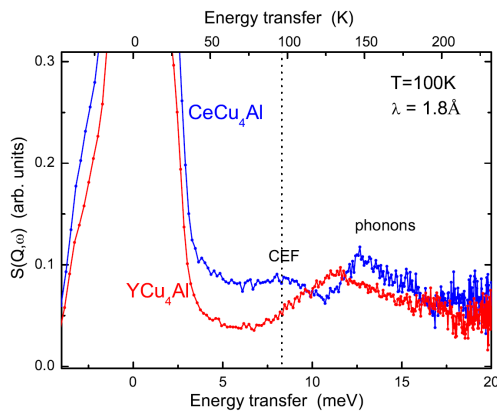


Fig. 4. Neutron time-of-flight spectra for  $\text{CeCu}_4\text{Al}$  and the reference compound  $\text{YCu}_4\text{Al}$  at the temperature of 100 K for wavelength of 1.8 Å.

#### 4. The $\text{CeCu}_4\text{Al}$ – $\text{CeNi}_4\text{Al}$ transition

Keeping the amount of Ce constant and substituting the Cu atoms by Ni drives the Kondo lattice  $\text{CeCu}_4\text{Al}$  to the FV  $\text{CeNi}_4\text{Al}$  [25]. The  $(\chi - \chi_0)^{-1}$  vs.  $T$  dependence (Fig. 5) indicates clearly that a fast change of the properties occurs at about  $x = 0.25$  for  $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_4\text{Al}$ . It is better visible if one plots the paramagnetic Curie–Weiss temperature  $\theta/4.5$  as a function of  $x$  (Fig. 6). According to the  $s$ – $d$  model [26] the Kondo temperature  $T_K = \theta/4.5$ . The dramatic changes in the magnetic susceptibility for  $x > 0.25$  are caused mainly by a change of the Ce valence. The transition to the FV state has been well visible in the XPS spectra (Fig. 7) of  $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_4\text{Ga}$  [27]. These compounds show similar properties as  $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_4\text{Al}$  but the HF state is more pronounced.

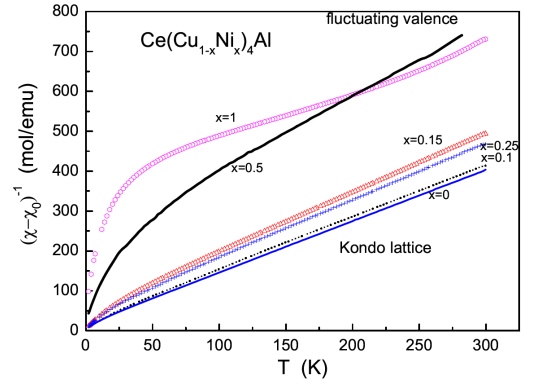


Fig. 5.  $(\chi - \chi_0)^{-1}$  vs.  $T$  dependence for  $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_4\text{Al}$ .

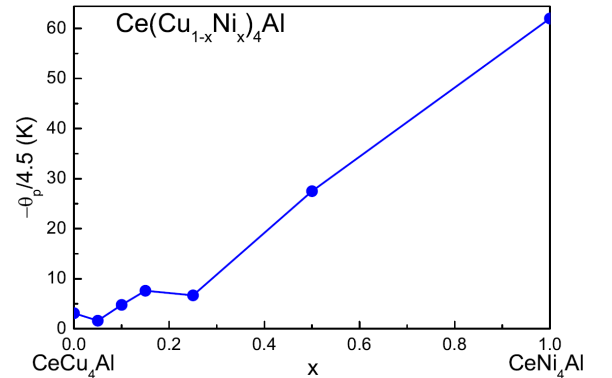


Fig. 6. Paramagnetic Curie–Weiss temperature  $\theta/4.5$  as a function of  $x$  for  $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_4\text{Al}$ .

In Fig. 7 a clear growth of the Ce  $3d4f^0$  with  $x$  can be noticed at energy of 914 eV within the Ce  $3d$  spectrum, which means a reduction of the  $f$ -occupancy for Ni rich compounds. In the valence band region it is possible to identify traces of the  $\text{Ce}(4f^1)$  states for  $x < 0.25$  — a clear corroboration of the localization deduced from the Ce( $3d$ ) spectra. For  $x > 0.2$  the Ni( $3d$ ) peak grows at the

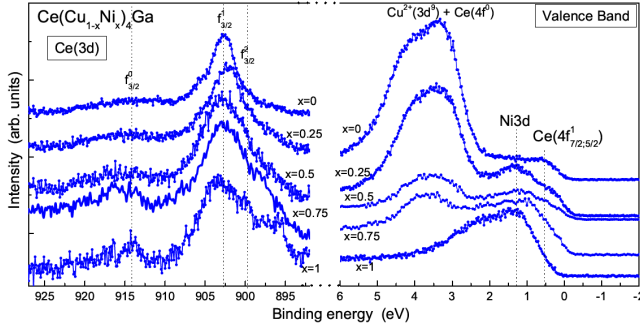


Fig. 7. XPS spectra of  $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_4\text{Ga}$  in the Ce  $3d$  and the valence band regions.

cost of the  $\text{Ce}(4f^1)$  and  $\text{Cu}(3d)$  peaks. It may suggest that an electron transfer occurs from  $\text{Ce}(4f^1)$  to  $\text{Ni}(3d)$  states, which can also explain the negligible magnetic contribution of Ni in the FV  $\text{CeNi}_4\text{Al}$  compound [28].

### 5. The $\text{CeNi}_4\text{Mn}$ – $\text{CeCu}_4\text{Mn}$ transition

As is depicted in Fig. 1,  $\text{CeNi}_4\text{Mn}$  and  $\text{CeCu}_4\text{Mn}$  represent a ferromagnetic and a spin-glass material, respectively.  $\text{CeNi}_4\text{Mn}$  is a soft ferromagnet [29], which due to the magnetic moment close to integer value and high degree of spin polarization was suspected to be a half metal — this was not confirmed in further studies. Among the systems drawn in Fig. 1, only this compound can exist in a modified structure (a cubic one) and the role of the disorder in this effect is still not fully understood. Simultaneously, disorder is often connected with the SG behavior. We have recently shown in complementary studies that  $\text{CeCu}_4\text{Mn}$  and  $\text{CeCuNi}_3\text{Mn}$  fulfill all the basic criteria characteristic of the SG behavior [30].

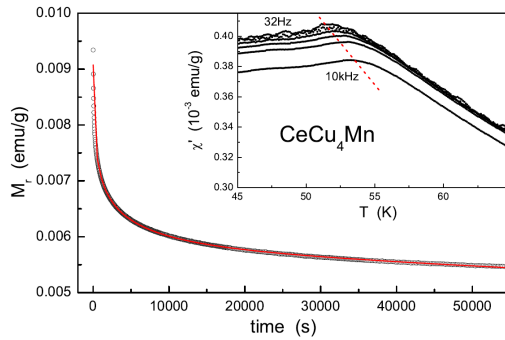


Fig. 8. Remanent magnetization decay for  $\text{CeCu}_4\text{Mn}$ . Inset: the real component of the ac magnetic susceptibility measured at various frequencies.

As can be seen in Fig. 8 and Fig. 9 the shift of the SG peak in the ac susceptibility as a function of frequency as well as the decay of the remanent magnetization are not visible for  $\text{CeNi}_4\text{Mn}$  in the case of the main peak at about 100 K; however, the frequency dependence may be hidden within the hump at 50 K and the strong tendency

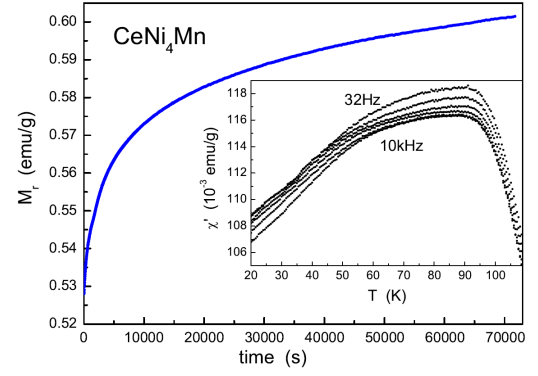


Fig. 9. Remanent magnetization decay for  $\text{CeNi}_4\text{Mn}$ . Inset: the real component of the ac magnetic susceptibility measured at various frequencies.

to disorder can be one of the sources of the structural sensitivity of the cubic  $\text{CeNi}_4\text{Mn}$  to small changes of the stoichiometry. A significant role of the disorder on the 3g sites in similar compounds has already been proved by neutron diffraction measurements [31].

### 6. The $\text{CeCu}_4\text{Mn}$ – $\text{CeCu}_4\text{Al}$ transition

Our initial measurements of the specific heat have shown that the electronic specific heat coefficient  $\gamma$ , changes from  $160 \text{ mJ K}^{-2} \text{ mol}^{-1}$  for the SG  $\text{CeCu}_4\text{Mn}$  to  $2300 \text{ mJ K}^{-2} \text{ mol}^{-1}$  for HF  $\text{CeCu}_4\text{Al}$ . The point is to find for which Al content the AF interactions between the Ce ions and the conduction electrons start to dominate over the Mn–Mn interactions responsible for the SG behavior. A strong enhancement of the effective mass is not visible in the specific heat up to  $x = 0.7$  (Fig. 10), however the  $\gamma$  value is already relatively large. Magnetic and transport measurements, including the magnetization relaxation and the frequency dependence of the ac magnetic susceptibility are being carried out for  $\text{CeCu}_4\text{Mn}_{1-x}\text{Al}_x$ .

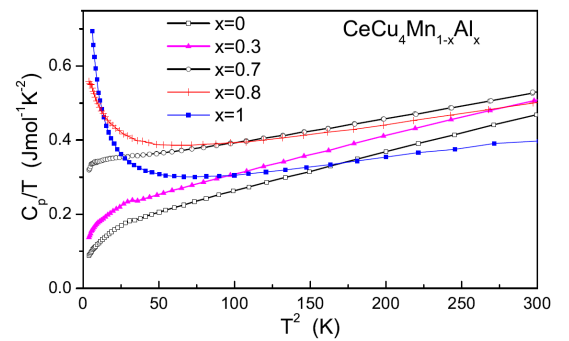


Fig. 10. Specific heat of  $\text{CeCu}_4\text{Mn}_{1-x}\text{Al}_x$ .

### 7. Conclusions

Transitions between the isostructural compounds  $\text{CeNi}_4\text{Mn}$ ,  $\text{CeNi}_4\text{Al}$ ,  $\text{CeCu}_4\text{Mn}$ , and  $\text{CeCu}_4\text{Al}$  have been

studied. For  $\text{Ce}_{1-x}\text{La}_x\text{Cu}_4\text{Al}$ , the localized character of the Ce ions enabled determination of the CEF parameters and their changes related to the reduction of the Ce ions concentration. A strong change of the interactions could be inferred from the values of the molecular field parameters and it may be inherent to the observed evolution between the Kondo lattice ( $x = 0$ ) and the impurity Kondo ( $x$  close to 1) physics.

Keeping the amount of Ce constant and substituting the Cu atoms by Ni drives the Kondo lattice  $\text{CeCu}_4\text{Al}$  to the fluctuating valence system  $\text{CeNi}_4\text{Al}$ . A survey of the valence band measured by XPS suggests that an electron transfer may occur from  $\text{Ce}(4f^1)$  to  $\text{Ni}(3d)$  states.

A gradual substitution of Ni in  $\text{CeNi}_4\text{Mn}$  by Cu reveals the spin-glass behavior and a significant role of the disorder on the 3g sites of the  $\text{CaCu}_5$ -type structure is especially well visible in the Mn-based compounds.

The role of Mn, disorder and Ce  $4f$  states is expected to be even more evident in the, being in progress, studies of the  $\text{CeCu}_4\text{Mn}_{1-x}\text{Al}_x$  and  $\text{CeNi}_4\text{Mn}_{1-x}\text{Al}_x$  compounds.

### Acknowledgments

This work was supported by the funds for science in years 2009–2011 as a research project no. N N202229537.

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